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Resins containing pendant chloromethyl groups were prepared by suspension co-polymerization techniques and functionalized with imidazole. This imidazole polymer, at various percent crosslinking and loading was used to examine the utility of Co(DPGB)$_2$·2MeOH as a reagent to investigate the existence of isolated functionalized sites in the resin. In this study, Co(DPGB)$_2$·2MeOH is attached to the imidazole containing polymer →

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20. Abstract (continued)

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Technical Report #1

A Versatile Approach for Investigating

Site Separation in Functionalized Organic

Polymers Containing Certain Donor Groups

by

Russell S. Drago and John H. Gaul

Prepared for publication in

Inorganic Chemistry

University of Illinois
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February 1, 1979

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A Versatile Approach for Investigating
Site Separation in Functionalized Organic
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Abstract

    Resins containing pendant chloromethyl groups were prepared by suspension co-polymerization techniques and functionalized with imidazole. This imidazole polymer, at various percent crosslinking and loading was used to examine the utility of $Co(DPGB)_2 \cdot 2MeOH$ as a reagent to investigate the existence of isolated functionalized sites in the resin. In this study, $Co(DPGB)_2 \cdot 2MeOH$ is attached to the imidazole containing polymer via axial coordination and the resulting polymer complexes studied by ESR. The ESR analysis of the coordinated cobalt centers yielded characteristic spectra of 1:1 and 2:1 imidazole-cobalt adducts depending on the crosslinking and loading of imidazole. The reaction of the polymer bound cobalt(II) complex with dioxygen has been investigated. Factors influencing the comparison of the oxygen affinity for the polymer bound complex with solution data are discussed.

Introduction

The modification of organic polymers by covalently attaching transition metal complexes constitutes a novel and active area of research. Much of the stimulation for research in this area has come from the advantages associated with converting selective homogeneous catalysts to heterogeneous polymer supported systems. Greater ease of removal of the catalyst from the reaction medium and a potential for working in flow systems are great advantages that polymer supported catalysts have over homogeneous ones. The advantages these materials have over the standard heterogeneous systems include higher selectivity, greater reproducibility, more efficient utilization of expensive metals and increased potential for catalyst tailoring via systematic variation of the ligands attached to the metal center.[1]

The change in reactivity that accompanies reported attachment of a homogeneous catalyst to an organic polymer have been unpredictable. In comparing results to the homogeneous system, some instances give similar behavior,[2] in other cases desirable changes in product distribution occur,[3] or enhanced reactivity is observed[4] and in still other cases reactivity is diminished or lost.[5] An understanding of these differences is thwarted by several major fundamental problems confronting an investigator working in the area. Establishing the structure of a complex on the polymer is a difficult task. Elemental analyses for carbon and hydrogen are useless for a hydrocarbon polymer while dilution makes it difficult to detect weak chromophores by many spectral techniques. When transition metal complexes are thought to be attached to polymers via a metal-monodentate ligand bond, it often becomes difficult to distinguish between coordination and physical entrapment. Exhaustive washing, needed to remove trapped species, may displace the complex from the ligand.

Another major problem in the area of polymer supported systems is that of site separation and an elucidation of the factors that influence this effect. One potential advantage of the polymer supported system involves preventing aggregation of coordinatively unsaturated species or other materials that decompose via intermolecular processes. For example, it has recently been reported that titanocene hydrogenation catalysts are deactivated by aggregation of the catalyst in solution.[6] Increased activity results from the polymer bound catalyst because the polymer backbone keeps the metal sites separated. On the other hand, when $RhCl[(C_6H_5)_3P]_2C_2H_4$ was added to a different type of resin functionalized with $(C_6H_5)_2PC_6H_4$-polymer, it was concluded[7] on the basis of the C_2H_4 and $(C_6H_5)_3P$ found in solution, that three of the polymer bound phosphines were coordinated to the rhodium. Many factors (for example, degree of substitution and cross linking) determine whether or not site separation is achieved in substituted polymers. There are several reviews on the subject and these contain apparent discrepancies leading to confusion about the factors that influence site separation. Different classes of functional groups on the polymer will show site separation under different conditions depending on the thermodynamic driving force for aggregation. Accordingly, a variety of systems will have to be investigated to gain an appreciation of the problem and methods must be developed for determining when site separation can be achieved in order to properly design catalyst systems.

Another major problem in the area of polymer bound reagents involves understanding the differences (compared to solution) that
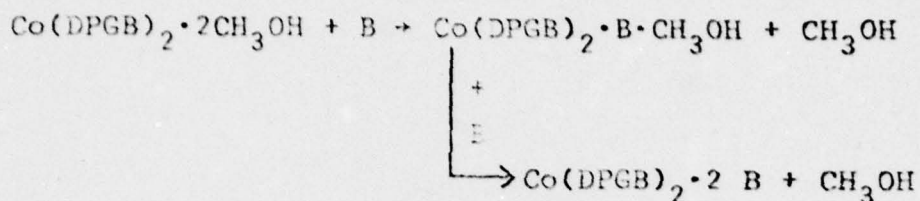
have been reported to occur in the coordination properties of
the metals. A procedure has been reported[8] for incorporating
an iron(II) heme into a polystyrene film that physically immobilizes
the ligand in the six coordinate complex so that the reversible
binding of CO observed in solution does not occur. On the other
hand, enhanced binding of O_2 is reported for tetraphenylporphyrin-
cobalt(II) coordinated to polystyrene bound imidazole in comparison
to the solution analogue.[9] An iron(II) porphyrin was coordinated
to a modified silica gel containing covalently attached 3-imidazoyl-
propyl groups. The resulting adduct is reported to reversibly bind
O_2 but it does so much less effectively than other iron(II)
systems.[10] It is not known whether these differences are
electronic, solvation, or entropic in origin.

In the course of investigations in this laboratory,[11] of the
epr spectra of a series of dioxygen adducts of cobalt(II) complexes,
a soluble cobalt(II) complex was found that formed paramagnetic
1:1 and 2:1 adducts with nitrogen donors. The complex is the
bis-methanol adduct of the complex

1.
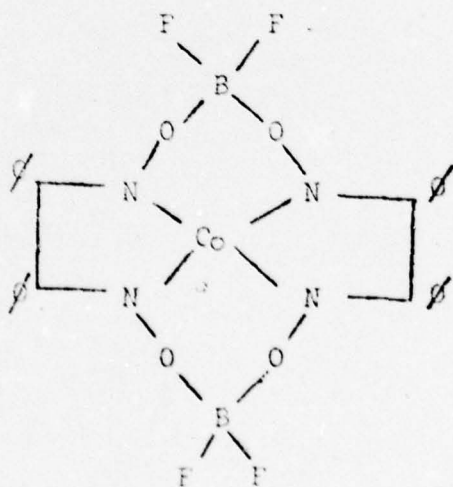
Abbreviating 1 as $Co(DPGB)_2$ the reactions with bases can be depicted as:

$$Co(DPGB)_2 \cdot 2CH_3OH + B \rightarrow Co(DPGB)_2 \cdot B \cdot CH_3OH + CH_3OH$$

$$\downarrow {}^{+}_{B}$$

$$\longrightarrow Co(DPGB)_2 \cdot 2\ B + CH_3OH$$

When one of the methanols is replaced by a nitrogen donor, a three line hyperfine is detected in the epr. When two identical nitrogen donors replace both methanols, a five line hyperfine is observed. Since the epr spectrum is readily observable at low metal concentrations, this complex should serve as a potentially useful indicator of site separation in polymers containing donor groups with a large isotopic abundance of nuclei with a nuclear spin quantum number $I > 0$. The epr spectra can also be used to demonstrate that the complex is coordinated and not physically trapped. Furthermore, a comparison of the hyperfine parameters for the polymer bound complex and solution analogue provide information regarding any changes in the strength of the donor-acceptor interaction that may be induced by the solid phase or desolvation.

In this article, we demonstrate the use of the reagent described above to elucidate the existence and absence of site separation for an imidazole donor covalently attached to some polystyrene polymers.

Experimental

Polymer Preparations

Gel Resins.

Imidazole containing resins were prepared by copolymerizing vinyl benzene (VB) with vinylbenzyl chloride (VBC) and divinyl benzene (DVB). The VBC monomer is a 60:40 mixture of the <u>meta</u> and <u>para</u> isomers and copolymerization of the above mixture results in crosslinked resins with pendant chloromethyl groups.

In general, the loadings in the polymer will be designated by the code number. The designations X and S refer to crosslinking and substitution. The numbers employed for all gel resins prepared with vinylbenzyl chloride have molar designations. For example, a resin prepared from 1 mole percent VBC, 10 mole percent DVB and 89 mole percent VB and designated GR-X10S1 where 1% of all the residues would contain chloromethyl groups.

In a typical preparation, GR-X15S6 resin was obtained by adding styrene 123 g (1.18 moles), vinylbenzyl chloride 14 g (0.09 moles), divinylbenzene 30 g (0.225 moles), benzoyl peroxide 0.75 g and 1.0 ml of mineral oil to 450 ml of warm water (80°) containing 4.5 g of soluble starch. The mixture was stirred at 400 rpm at 80°C for 24 hr. The reaction mixture was cooled, passed through a fine mesh (#100) sieve, washed with organic solvents and H_2O (H_2O, H_2O-MeOH, THF, or CH_2Cl_2), then dried at 80°C overnight. The resin GR-X10S1 analyzed for 0.33% chlorine and GR-X15S6 contained 1.92% chlorine.

Macroreticular Resins

Macroreticular polystyrene[14] was slurried in 100 g chloromethyl-ethyl ether in a dry atmosphere. Tin(IV) chloride, 5 ml, in 33 g chloromethylethyl ether (CME) was added with cooling. (CAUTION: Chloromethylethyl ether is extremely carcinogenic). Stirring continued in an ice bath for 10 min, and at room temperature for 50 min. Aqueous dioxane (1:3 v/v), 150 ml, was then added and stirring continued for 1 hr. At this point the resin was filtered and washed with large quantities of H_2O, 2M HCl, H_2O, H_2O-dioxane, dioxane, dioxane-methanol, and finally methanol. The polymer was dried at 80°C. The loadings for the macroreticular resins are reported in terms of percent by weight. Reaction with CME results in chloromethyl groups being attached at the para position. The extent of chloromethylation is hard to control. The chloromethylated macroreticular resin MRX20S20 (weight basis) contained 4.55% Cl.

Imidazolation of chloromethylated resin.

Once the chloromethylated resin is obtained, it is reacted with the lithium salt of imidazole to obtain the resin bound analog of N-methylimidazole. In a typical preparation, 20 g of the above chloro-methylated macroreticular resin and 6.8 g imidazole were added to a 500 ml round bottom flask with sidearm. The mixture is slurried in 200 ml of THF under an argon atmosphere and 62.5 ml n-butyl lithium (1.6 M in hexane) was added at 0°C. The slurry was allowed to warm to room temperature, and heated to reflux. Refluxing continued for 16 hr at which time the resin was cooled, Sohxlet extracted with THF for and then dried in vacuo. Analysis for MRX20S20 gave 2.97% N and Cl. MRX20S20 contained 1. N and MRX1051 0.25%.

Preparation of Co(DPGH)₂·2MeOH. Bis(diphenylglyoximato)cobalt(II). [Co(DPGH)₂] was prepared according to a published procedure.[15] This

complex was capped in a fashion similar to that reported in the literature.[8] Freshly distilled $BF_3 \cdot OEt_2$ (10 ml) was added to 100 ml of ethyl ether and the resulting solution deoxygenated. $Co(DPGH)_2$ (5.0 g) was added under an argon atmosphere and the slurry stirred at room temperature two days. Deoxygenated methanol (50 ml) was then added and stirred several hours. The slurry was filtered and washed with methanol until the filtrate was colorless (50-75 ml). The orange powder was pumped to dryness.

Calc. for $C_{30}H_{28}N_4O_6B_2F_4Co$: C, 51.68; H, 4.09; N, 8.04; Co, 8.45. Found: C, 51.35; H, 3.86; N, 8.27; Co, 8.11.

Metal Incorporation into the Polymer

The cobalt complex was incorporated into base containing resins by the following method. $Co(DPGB)_2 \cdot 2MeOH$ (0.70 g) and 1.0 g of imidazole containing resin were added to a 250 ml three necked round bottom and flushed with argon. 100 ml of dry degassed THF was syringed in and the resin stirred at room temperature for two days. The resin was filtered washed with THF in a Schlenk type Sohxlet extractor 24 hr and then dried in vacuo.

EPR Studies

Samples for epr were prepared by adding the dry resin to an epr tube with vacuum teflon fittings. The tubes were evacuated and filled with argon several times. When the dioxygen adducts of the coordinate polymer cobalt complexes were desired, the epr tube was cooled to dry ice-acetone temperatures and the atmosphere replaced with pure oxygen. The beads were allowed to equilibrate with oxygen in this fashion for at least one hr. Samples of the parent complexes for epr analysis were prepared by dissolving in dry degassed CH_2Cl_2/toluene solvent (1:1 v/v) in volumetric flasks in a dry inert atmosphere box. Solutions were added to the epr tubes and the vacuum fittings closed off. Alternatively, the degassed solvent mixture could be distilled directly onto the cobalt sample weighed into an epr tube.

The epr spectra were collected on a Varian model E-9 spectrometer equipped with a Hewlett-Packard frequency counter. Cooling was provided by cold nitrogen gas, producing a probe temperature of $\sim -180°C$. The field was calibrated using a Varian weak pitch sample, $g = 2.0070$.

The spectra of the $Co(DPGB)_2 \cdot$ base adducts are axial in appearance and result in relatively sharp well-defined spectra. Upon coordination of metal complexes to coordinate polymers, a certain amount of general broadening is seen, causing a reduction in the resolution of hyperfine. This may be due to a certain amount of polymer chain motion even at low temperature or to a lack of magnetic dilution in certain cases. For this reason, second order corrections[16] to the epr parameters were ignored since it was felt they would provide no additional useful information. Best values for $\frac{h c}{g_{//} \beta}$ and $A_{//}$ were obtained from the most well defined signals in the parallel region.

Results and Discussion

Adducts of Oxime Complexes of Cobalt(II)

Bis-diphenylglyoximato cobalt(II) readily forms a 1:1 adduct that exists in solution in a monomer-dimer equilibrium. Dimerization occurs through coordination of one of the oxime oxygens to the cobalt of another complex. The dimer is diamagnetic, owing to an antiferromagnetic interaction between the cobalt centers. Addition of more base, stronger than the oxime oxygen, cleaves the dimer with ready formation at room temperature of the paramagnetic 2:1 adduct.

The diamagnetic nature of the dimeric 1:1 adduct is unsuitable for our purposes. We would like to be able to tell under what resin conditions 1:1 adducts are favored over 2:1 adducts. Ideally, the 1:1 adduct should be paramagnetic and have a characteristic epr spectrum. Dimer formation can be prevented if the basicity of the oxime oxygens can be reduced sufficiently. This reduction of the oxime oxygen

basicity can be achieved with a concomittant bonus in increased

cobalt acidity by capping the complex with tetrahedral BF_2 groups,

compound 1. This BF_2 capped cobalt complex is so acidic that it is

most readily isolated as 2:1 base adducts. We chose the weak base

methanol as the starting adduct because it is readily replaced.

Addition of 1 equivalent of a/base stronger than methanol displaces
^{neutral}

one methanol and forms a mixed base-methanol six coordinate complex.

Further addition of strong base gives the trans 2 base to 1 cobalt(II)

adduct, readily at room temperature. The formation of both 1:1 and

2:1 base adducts in discrete steps is a particularly attractive

feature of this complex for studying site separation in a polymer.

The solution species can be studied separately and compared with

the species prepared on the polymer.

Low spin, d^7, tetragonal complexes of cobalt(II) are particularly

well suited for epr studies. The unpaired spin resides in the $3d_{z^2}$

orbital and thus axial coordination by either one or two bases will

perturb this electron directly and influence the epr spectrum. Since

coordinated methanol does not exhibit nuclear hyperfine splitting in

the epr, the mixed 2:1 adduct, where one of the bases is a nitrogen

donor, should exhibit a three line superhyperfine pattern. The

symmetrical 2:1 adduct gives rise to a five line superhyperfine pattern.

Electron nuclear hyperfine in the perpendicular region of these

compounds is usually small (~10 gauss) and therefore superhyperfine is

more difficult to observe on these peaks. In addition, epr spectra

of low spin Co(II) complexes are often broad owing to relaxation mechan-

isms which involve low lying excited states. This results in more spin

orbit coupling which causes shorter spin relaxation times. Consequently,

superhyperfine cannot be measured accurately in the perpendicular region.

The parallel region, however, is characterized by hyperfine couplings

on the order of 60 to 100 x 10^{-4} cm^{-1} and can be accurately measured.

The epr spectrum of Co(DPGB)$_2$·2CH$_3$OH is illustrated in Figure 1 and the spectral characteristics of the N-methylimidazole base adducts are summarized in Table 1.

Table 1

Frozen Solution[a] Epr Parameters for Co(DPGB)$_2$·2CH$_3$OH and the Complexes Formed by Displacing One and Two Methanols with N-methylimidazole

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (x10^{-4}cm)	$A_{\perp}$ (x10^{-4}cm)	A_{Co-N} (x10^{-4}cm)
Co(DPGB)$_2$·2MeOH	2.010	2.26	105	10	0
Co(DPGB)$_2$·B[b]·MeOH	2.002	2.27	93.5	10	14.5
Co(DPGB)$_2$·B$_2$[b]	2.016	2.26	74.0	14	18.5

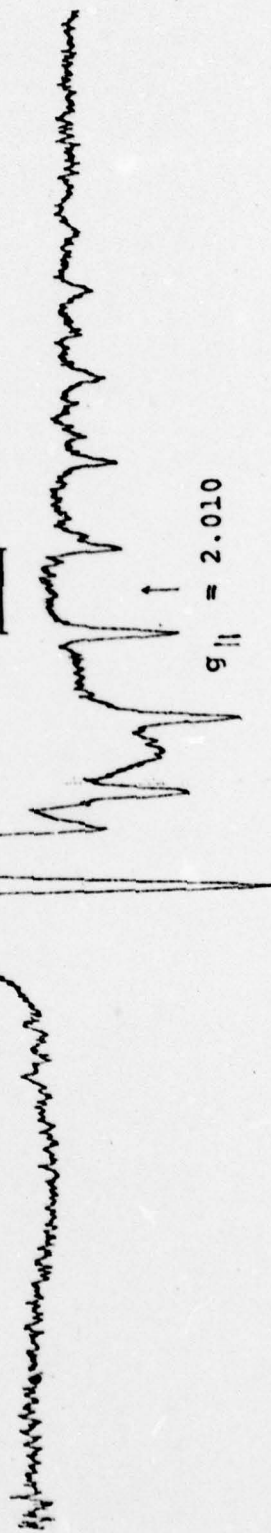[a]Frozen toluene/CH$_2$Cl$_2$ glass at liquid N$_2$ temperature.

[b]B refers to the base N-Methylimidazole.

Substantial differences exist in both the A values and the A_{Co-N} hyperfine values for the different adducts which should permit one to determine the coordination sphere of imidazole substituted polymer bound Co(DPGB)$_2$.

$g_\perp = 2.26$

$A_\parallel = 105 \times 10^{-4}$ cm^{-1}

$g_\parallel = 2.010$

Binding of Co(DPGB)$_2$ to Polymer Bound Imidazole

Three different imidazole substituted resins were prepared to investigate the question of site separation; GR-X10S1, GR-X15S6 and MR-X20S20.[13] The choice of resins offers a variation in the three controlling factors: crosslinking, substitution and polymer type. In all cases THF was selected as the solvent for complex incorporation. Any increase or decrease in site interactions from swelling of the polymer by solvent or other solvent effects is thus held constant. Incorporation of Co(DPGB)$_2$ into these three resins followed by thorough anaerobic extraction yielded a red brown solid resin.

The epr spectra of the complex bound to these three resins and measured at liquid nitrogen temperature are given in Figures 2, 3 and 4. The epr parameters are reported in Table 2.
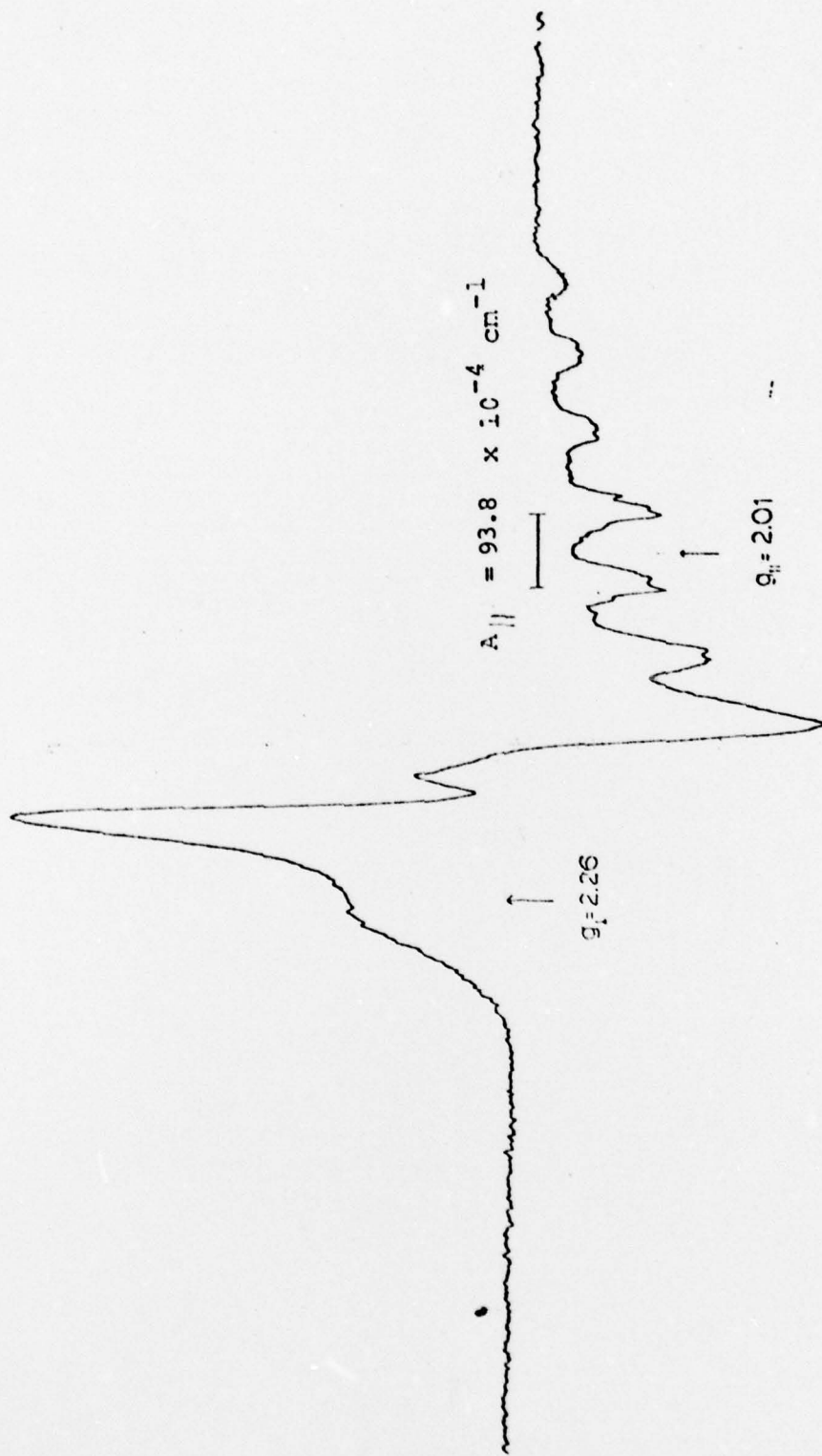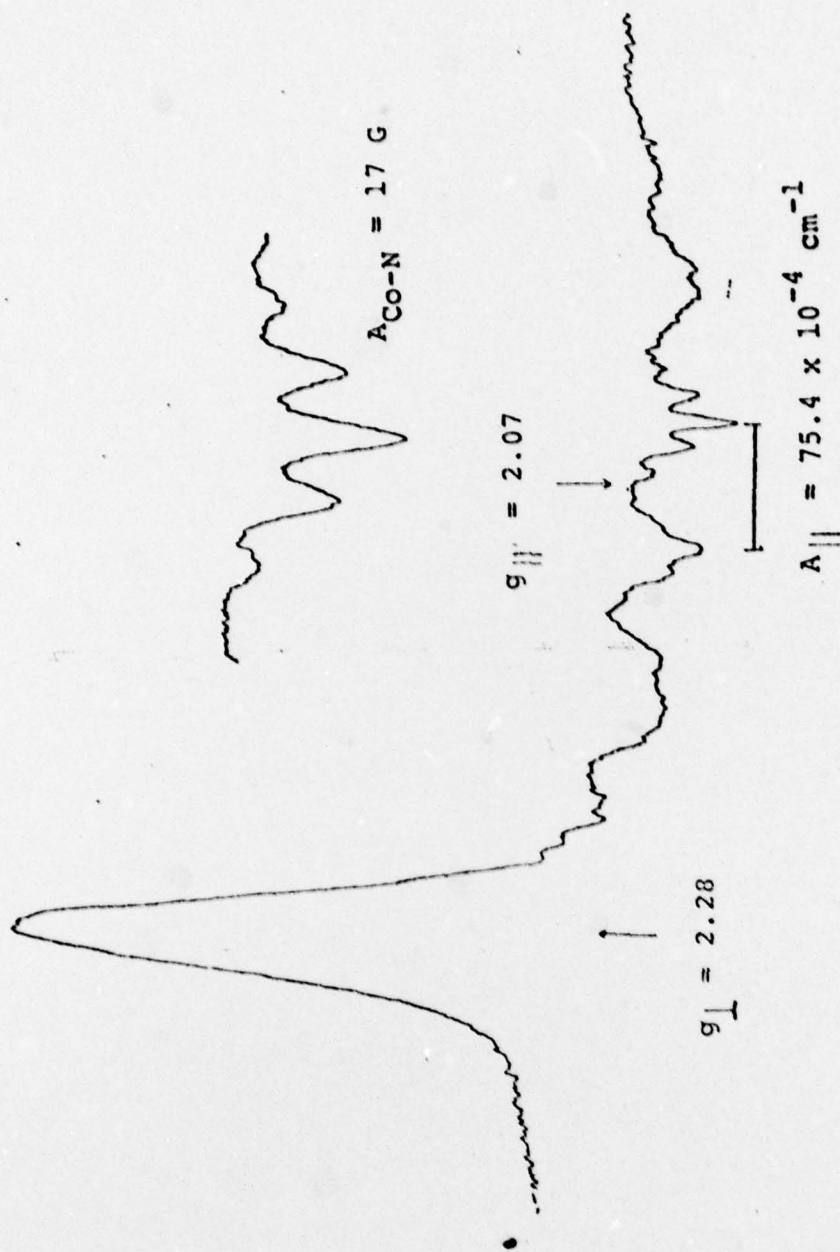
Table 2
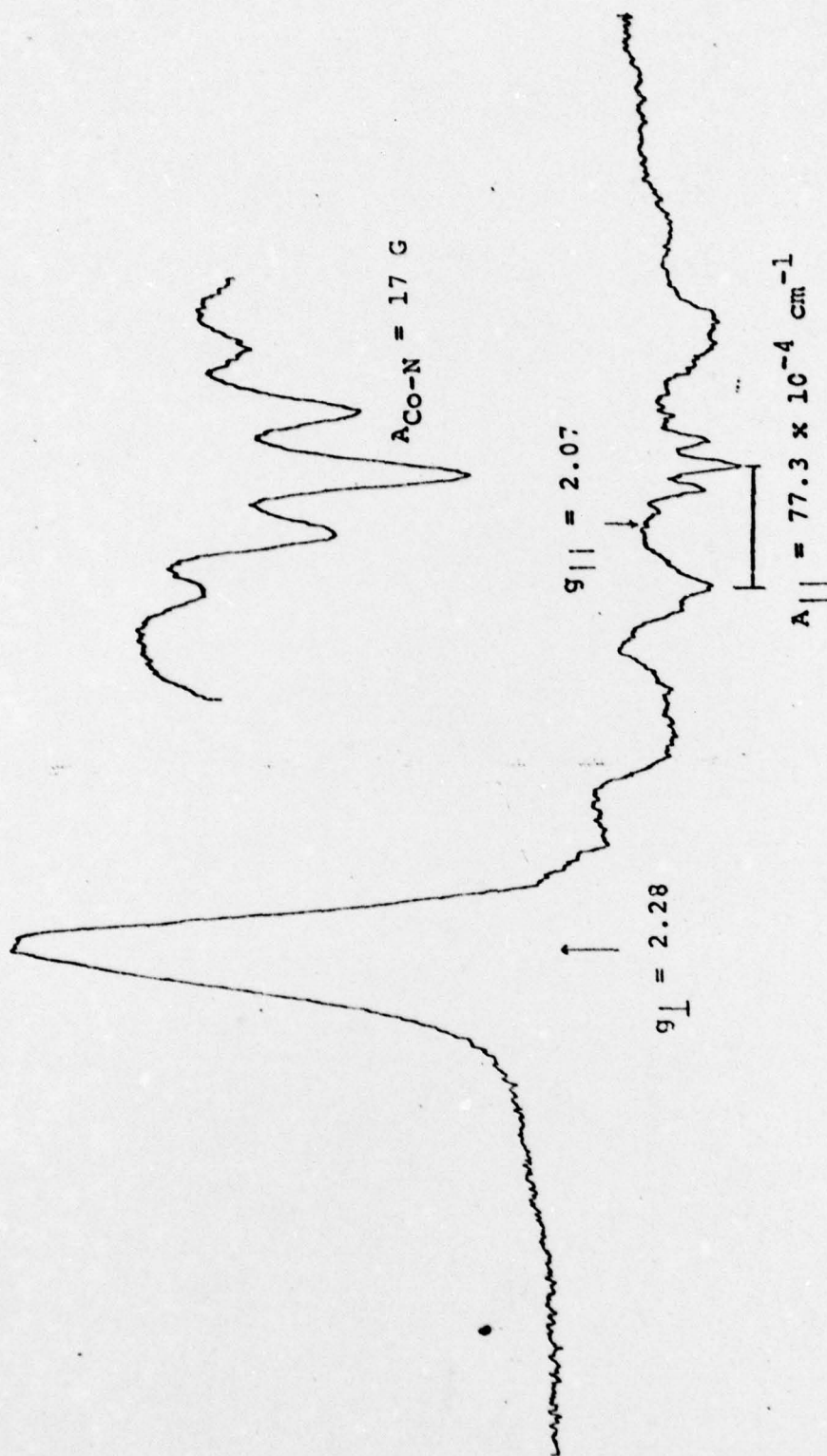
Epr Parameters for Polymer Bound Co(DPGB)$_2$ Complexes

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (x10^{-4}cm)	$A_{\perp}$	A_{Co-N} (x10^{-4}cm)
GR-X10S1-[P]-CH$_2$Imid-Co(DPGB)$_2$·MeOH	2.01	2.26	93.8	--	$\sim$10
GR-X15S6-[P]-(CH$_2$Imid)$_2$-Co(DPGB)$_2$	a	2.28	75.4	small	17
MR-X20S20-[P]-(CH$_2$Imid)$_2$ Co(DPGB)$_2$	a	2.28	77.3	small	17

[a] Because of overlap with $g_{\perp}$ and broadening of the resonances at high field, it was difficult to locate the center of the parallel resonances.

$A_{||} = 93.8 \times 10^{-4}\ cm^{-1}$

$g_{||} = 2.01$

$g_\perp = 2.26$

$A_{Co-N} = 17$ G

$g_{||} = 2.07$

$A_{||} = 75.4 \times 10^{-4}$ cm^{-1}

$g_{\perp} = 2.28$

$A_{Co-N} = 17$ G

$g_{||} = 2.07$

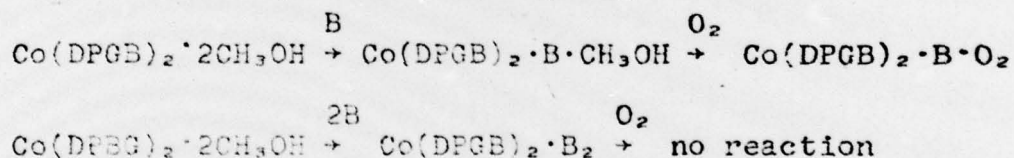$A_{||} = 77.3 \times 10^{-4}$ cm^{-1}

$g_{\perp} = 2.28$

The spectra are of the same general shape as that of the unbound, soluble, imidazole complexes. The parallel and perpendicular regions and cobalt nuclear hyperfine are evident in all four spectra. The line widths of the polymer bound complexes are characteristically broadened with the simultaneous loss of resolution, especially in the perpendicular region. The g and A values for the mixed 2:1 base-CH_3OH adducts and symmetrical 2:1 adducts are given in Table 1 and can be compared with the same parameters obtained for the polymer spectra reported in Table 2. The $g_{||}$ and $g_{\perp}$ values are not diagnostic. Considering the broadening and uncertainty of peak position, these values could be considered the same within experimental error since they differ only by ~ 2-3%. The values that seem to best distinguish the complexes are the $A_{||}$ values and the superhyperfine coupling constants A_{Co-N}, from the nitrogen bases. On the basis of these results, we conclude that the complex $Co(DPGB)_2 \cdot 2CH_3OH$ on GR-X10S1 has one CH_3OH displaced and is essentially coordinated to one of the polymer bound N-alkylimidazoles. The spectrum of the complex coordinated to this resin reveals poorly characterized hyperfine from the axially coordinated, nitrogen donor ligands. However, the observed values of $A_{||} = 93.8 \times 10^{-4}$ cm^{-1} and $A_{Co-N} \cong 10 \times 10^{-4}$ cm^{-1} compare favorably with those listed in Table 1 for the mixed N-methylimidazole-methanol complex. This clearly establishes site separation in the displacement reaction of methanol from $Co(DPGB)_2 \cdot 2CH_3OH$ in this resin. On the other hand, the spectra of the complex on the GR-X15S6 and MR-X20S20 resin clearly show the hyperfine splitting pattern expected for two axially coordinated nitrogen bases on a low spin, d^7, tetragonal cobalt(II) center. The $A_{||}$ values of 75.4×10^{-4} cm^{-1} and 77.3×10^{-4} cm^{-1} for the gel and macroreticular resin compare favorably with those for the symmetrical 2:1 nitrogen base-$Co(DPGB)_2$ complex reported in Table 1. Thus, site separation

is not achieved toward $Co(DPGB)_2$ in these polymers.

Dioxygen Binding in the Metal Substituted Polymers

The adducts of $Co(DPGB)_2 \cdot 2CH_3OH$ exhibit somewhat different behavior towards oxygen as compared to Schiff base and macrocyclic cobalt complexes. Many of these latter complexes bind one base readily to form 5-coordinate complexes which then bind O_2 reversibly. When these compounds form 2:1 base adducts (often with a large excess of base), this second base is displaced upon exposure to O_2 to give the base-dioxygen adduct. The $Co(DPGB)_2$ complex does not behave this way. The dimethanol complex readily binds one base (displacing one methanol) to form the unsymmetrical 2:1 adduct which can then bind O_2 by displacing the second methanol. However, exposure of the symmetrical 2:1 adduct of N-methylimidazole to O_2 does not yield the dioxygen adduct. That is, when B is N-methylimidazole we can write:

$$Co(DPGB)_2 \cdot 2CH_3OH \xrightarrow{B} Co(DPGB)_2 \cdot B \cdot CH_3OH \xrightarrow{O_2} Co(DPGB)_2 \cdot B \cdot O_2$$

$$Co(DPBG)_2 \cdot 2CH_3OH \xrightarrow{2B} Co(DPGB)_2 \cdot B_2 \xrightarrow{O_2} \text{no reaction}$$

This chemistry can be used to provide some additional information regarding our imidazole substituted resins. On the basis of the solution behavior, we might expect that only the unsymmetrical base-methanol 2:1 complexes on the resin will interact with oxygen while the symmetrical 2:1 complexes of N-methylimidazole will not. The ESR spectrum for $Co(DPGB)_2 \cdot N\text{-}CH_3Imid \cdot O_2$ is illustrated in Figure 5. The signal shape is intense and dramatically different from the spectra of the base adducts. Two g values are evident along with the eight line cobalt nuclear hyperfine.
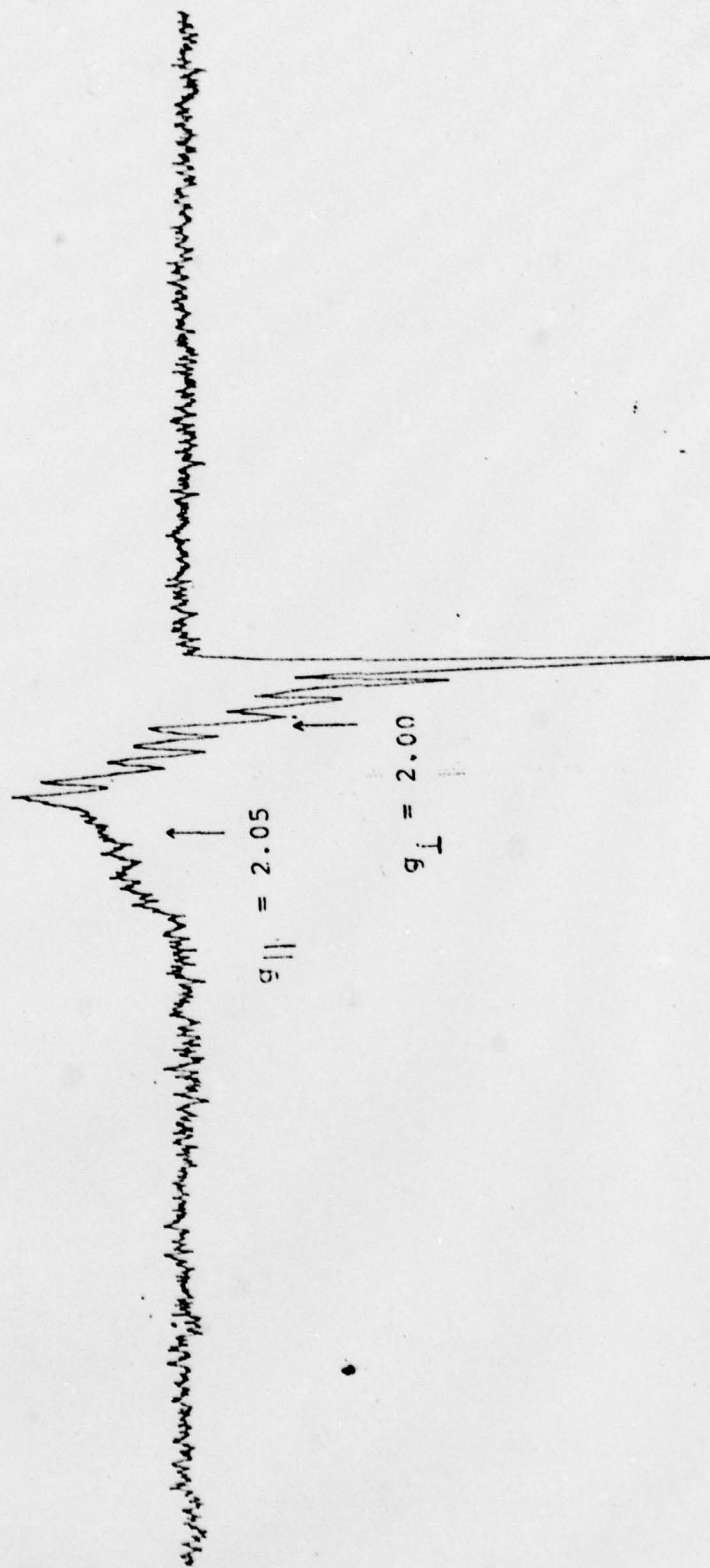
Exposure of GR-X10S1 to oxygen results in virtually complete disappearance of the original signal and the appearance of the O_2 adduct signal. This is in keeping with our conclusion that the $Co(DPGB)_2$ is bound to the resin through only one imidazole. A different situation results for GR-X15S6 and MR-X20S20. In both cases, we concluded earlier that most of the cobalt is bound to two imidazoles. However, some small percentage of cobalt centers bound to only one imidazole could exist.   This is very clearly borne out by the epr spectra of these resins after exposure to oxygen. The O_2 adduct gives rise to a very intense signal so a direct comparison of the O_2 signal intensity to that of the residual base adduct is not

possible. However, intense signals that can be attributed to deoxy cobalt(II) centers are found in both GR-X15S6 and MR-X20S20, but not in GR-X10S1. Clearly, very incomplete conversion of the former two polymers to the O_2 adduct occurs in keeping with the conclusion that most of the cobalt centers have two imidazole donors bound to them in the polymer. A larger percentage of O_2 adduct formation occurs with the macroreticular resin than with the gel resin. This would suggest that there are more unsymmetrical 2:1 adducts and more site separation in MR-X20S20 than in GR-X15S6. The following conclusions are definitive. Site separation, as evidenced by formation of the unsymmetrical 2:1 base adduct, is achieved in a gel resin prepared in this study at a level of 1% substitution. Neither GR-X15S6 nor MR-X20S20 allow large amounts of site separation even though they are highly crosslinked. In both of these resins, the symmetrical 2:1 base adduct is the predominant species implying extensive site interactions. Formation of some O_2 adduct in both resins does indicate that there are some separated sites.

The bis-methanol adduct used in this work can be used to probe site separation in a functionalized polymer containing donor groups that give rise to superhyperfine splitting. Functionalized polymers containing other types of donors can be studied using the bis-acetonite adduct of Co(DMGB)$_2$. This material can be prepared by recrystallization of the bis-methanol adduct from acetonitrile. The complex Co(DMGB)$_2 \cdot$2CH$_3$CN exhibits well resolved nitrogen superhyperfine coupling and the changes in the spectra upon coordination to a functionalized polymer can also be used to probe site separation.
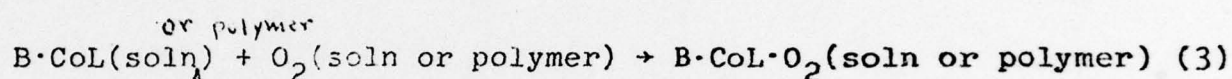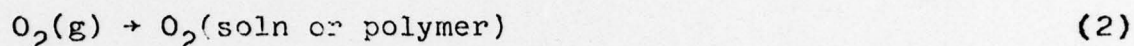
Comparison of Solution and Polymer Bound Reactivities.

The comparison of the reactivity of a substrate in solution and on a polymer is a very important consideration for the area of supported reagents. Such comparisons[2-5] have revealed some interesting contrasts and similarities. With regards to the binding of dioxygen, two reports[9,10] of enhanced affinity for coordination of O$_2$ by polymer bound substrates have appeared but causes for the proposed enhanced affinities have not been established. Enhancement could be due to entropic factors, a difference in metal oxygen bond strength in the two media, solvation differences for the adduct in the different media or a combination of these effects. Unfortunately, the epr spectra of the polymer bound O$_2$ adducts studied in this work are broadened to such an extent that it is difficult to infer whether or not the electronic structure of bound O$_2$ differs slightly for the two conditions. Closer consideration of the evidence for enhanced binding of O$_2$ by the metal complex on the polymer reveals that this reported conclusion has not been established in a completely rigorous fashion. Qualitative comparisons have been based on the relative magnitudes of the P$_{\frac{1}{2}}$O$_2$ values at a given temperature. For solution and polymer

supported conditions, this quantity could be dominated by factors other than the metal-dioxygen adduct stability. The $P_{\frac{1}{2}} O_2$ values in solution relate to the equilibrium constant for the process

$$B \cdot CoL(soln) + O_2(g) \rightarrow B \cdot CoL \cdot O_2(soln) \qquad (1)$$
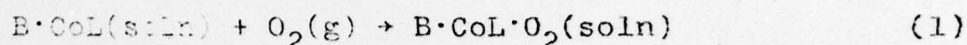
However, this is a net equilibrium constant for the two independent processes:

$$O_2(g) \rightarrow O_2(soln\ or\ polymer) \qquad (2)$$

$$B \cdot CoL(soln)^{or\ polymer} + O_2(soln\ or\ polymer) \rightarrow B \cdot CoL \cdot O_2(soln\ or\ polymer) \quad (3)$$

Thus, as long as the medium is held constant, $P_{\frac{1}{2}} O_2$ values can be compared to provide information on metal-dioxygen interactions. However, the comparison of $P_{\frac{1}{2}} O_2$ values for systems studied in different media will contain contributions from the equilibrium constant for equation (2) above. Labelling the equilibrium constants for equations (1), (2) and (3) above as K_1, K_2, and K_3 respectively, we note that $K_1 = K_2 \cdot K_3$ and that K_2 is independent of the complex. Unless information is available regarding the thermodynamic data for equation (2), an interpretation of $P_{\frac{1}{2}} O_2$ data (on systems investigated in different media) to yield information regarding the metal-dioxygen interaction is not possible. Even with polymer variation, the polymer bound data must be corrected for the distribution constant involving

$$O_2(g) \rightarrow O_2(polymer)$$
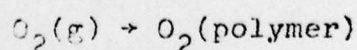
before trends in metal binding or metal-O_2 solvation by the medium can be deduced.

FIGURE CAPTIONS

Figure 1.   ESR spectra of Co(DPGB)$_2$·2MeOH in frozen toluene/CH$_2$Cl$_2$ glass at liquid N$_2$ temperature.

Figure 2.   ESR spectrum of Co(DPGH)$_2$·2MeOH attached to the imidazole polymer GR-X10S1 at liquid N$_2$ temperature.

Figure 3.   ESR spectrum of Co(DPGB)$_2$·2MeOH attached to the imidazole polymer GR-X15S6 at liquid N$_2$ temperature.

Figure 4.   ESR spectrum of Co(DPGB)$_2$·2MeOH attached to the imidazole polymer MR-X20S20 at liquid N$_2$ temperature.

Figure 5.   ESR spectra of Co(DPGB)$_2$·N-CH$_3$ imidazole·MeOH exposed to an oxygen atmosphere at liquid N$_2$ temperature in a toluene/CH$_2$Cl$_2$ glass.

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(12) Vinylbenzyl chloride was a gift from the Dow Chemical Co., Midland, Michigan.

(13) GR stands for gel resin and MR macroreticular. The % cross-linking follows X and the % substitution follows S. Cross-linking and substitution are in molar %. X15 (molar) = X20 (% by weight) and S6 (molar) = S8 (% by weight).

(14) Samples of this resin were kindly provided to us by Professor Carl Brubaker who obtained them from commercial sources.

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